# Preparation and Crystal Structure of $[Mo\{S_2P(OMe)_2\}_3]$ and an Improved Route to $[MoCl_3(thf)_3]$ †

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The complex $[MoCl_3(thf)_3]$ (thf = tetrahydrofuran) is prepared in high yield by the tin reduction of $[MoCl_4(thf)_2]$ in thf. It reacts with $[NH_4][S_2P(OMe)_2]$ in dry methanol to give $[Mo\{S_2P(OMe)_2\}_3]$ which crystallizes in the space group $C2/c$ with $a = 14.342(5)$, $b = 11.239(5)$, $c = 12.945(4)$ Å, $\beta = 97.12(1)°$, and $Z = 4$. 2 453 Reflections gave $R = 0.039$. The molybdenum is pseudo-octahedral and the complex has overall $C_2$ symmetry. The Mo–S average distance is 2.507(2) Å.

Monomeric molybdenum(III) complexes with purely sulphur ligation are virtually unknown, as reaction of molybdenum(III) precursors with simple thiols generally leads to thiolato- or sulphido-bridged oligomers. There has been some discussion as to the existence of monomeric $[Mo(S_2CNR_2)_3]$ (R = alkyl) complexes,[1] and our own attempts to prepare $[Mo(S_2CNR_2)_3]^+$ by reaction of $[MoCl(S_2CNR_2)_3]$ with $Tl[BF_4]$ led only to $[Mo(S_2CNR_2)_4][BF_4]$.[2] We decided the investigate the analogous dithiophosphinate systems and we here report the preparation of $[Mo\{S_2P(OMe)_2\}_3]$ in reasonable yield by reaction of $[MoCl_3(thf)_3]$ (thf = tetrahydrofuran) with $[NH_4][S_2P(OMe)_2]$ in methanol. The complex has been previously reported as a product of the reaction of $[MoCl_2(CO)_4]$ with $[NH_4][S_2P(OMe)_2]$ and aryl azides,[3] but the yields are not high and the synthesis is indirect.

The complex $[MoCl_3(thf)_3]$ is an excellent starting point for the synthesis of molybdenum(III) complexes. However, the reported synthesis[4] using zinc as reductant for $[MoCl_4(thf)_2]$ is difficult to control and the product can easily be contaminated with intensely coloured by-products. The use of tin powder as reducing agent is much more convenient. The product is obtained in high yield (~70%) and generally free of coloured contaminants.

In view of the paucity of structural data on monomeric molybdenum(III) complexes with sulphur donors we have also undertaken the *X*-ray crystal structure determination of $[Mo\{S_2P(OMe)_2\}_3]$.

## Results and Discussion

*Crystal and Molecular Structure of* $[Mo\{S_2P(OMe)_2\}_3]$.—Brilliant red crystals of the complex were obtained from dichloromethane–Pr$^i$OH. Atomic parameters are shown in Table 1 and selected bond lengths and angles are summarised in Table 2. An ORTEP view of the molecule is presented in the Figure, showing the atom labelling scheme.

Table 1. Atomic positional parameters for $[Mo\{S_2P(OMe)_2\}_3]$

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Mo | 0.000 00 | 0.156 25(7) | 0.250 00 |
| P(1) | 0.178 6(1) | 0.027 9(2) | 0.354 2(1) |
| P(2) | 0.0000 | 0.432 2(2) | 0.2500 |
| S(1) | 0.121 2(1) | 0.007 7(2) | 0.207 2(1) |
| S(2) | 0.096 2(1) | 0.136 4(2) | 0.424 0(1) |
| S(3) | −0.089 6(1) | 0.326 9(2) | 0.312 9(1) |
| O(1) | 0.197 3(4) | −0.093 3(4) | 0.412 4(4) |
| O(2) | 0.282 9(3) | 0.070 7(4) | 0.364 6(4) |
| O(3) | 0.048 8(4) | 0.526 0(4) | 0.327 5(4) |
| C(1) | 0.119 3(6) | −0.168 4(7) | 0.431 1(7) |
| C(2) | 0.307 4(6) | 0.185 1(7) | 0.324 7(7) |
| C(3) | 0.114 0(6) | 0.486 5(7) | 0.416 8(6) |

Table 2. Selected bond lengths (Å) and angles (°) for $[Mo\{S_2P(OMe)_2\}_3]$

| | | | |
|---|---|---|---|
| Mo–S(1) | 2.520(2) | P(2)–S(3) | 1.993(2) |
| Mo–S(2) | 2.501(2) | P(2)–O(3) | 1.560(5) |
| Mo–S(3) | 2.500(2) | O(1)–C(1) | 1.446(10) |
| P(1)–S(1) | 1.990(2) | O(2)–C(2) | 1.446(9) |
| P(1)–S(2) | 1.991(3) | O(3)–C(3) | 1.463(9) |
| P(1)–O(1) | 1.564(5) | | |
| P(1)–O(2) | 1.562(5) | | |

| | | | |
|---|---|---|---|
| S(1)–Mo–S(1′) | 97.1(1) | S(2)–Mo–S(3)<br>S(2′)–Mo–S(3′) | 91.3(1) |
| S(1)–Mo–S(2)<br>S(1′)–Mo–S(2′) | 79.7(1) | S(2)–Mo–S(2′) | 169.8(1) |
| S(1′)–Mo–S(3)<br>S(1)–Mo–S(3′) | 167.4(1) | S(2)–Mo–S(3′)<br>S(2′)–Mo–S(3) | 96.5(1) |
| S(1)–Mo–S(2′)<br>S(1′)–Mo–S(2) | 93.5(1) | S(3)–Mo–S(3′) | 79.8(1) |
| S(1′)–Mo–S(3′)<br>S(1)–Mo–S(3) | 92.3(1) | S(1)–P(1)–S(2) | 107.8(1) |
| | | S(3)–P(2)–S(3′) | 107.2(1) |

Primed atoms are related to labelled atoms by the two-fold rotation about the Mo–P(2) vector.

The geometry of the complex is pseudo-octahedral, with deviations from the octahedral limit ascribable to constraints imposed by the three four-membered Mo–S–P–S rings. The average Mo–S bond distance of 2.507(2) Å is very similar to those found in $[\{Mo(NC_6H_4CH_3)(\mu_3\text{-}S)[S_2P(OEt)_2]\}_4]$[5] and $[Mo_2O_3(NH)\{S_2P(OEt)_2\}_2]$.[6] Both the Mo atom and P(2) of a dithiophosphinate ligand lie on a crystallographic two-fold axis, and the molecule has overall $C_2$ molecular symmetry. The bond lengths and angles within the dithiophosphinates lie within the range found for other complexes of these ligands.[4,5]

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† Tris(*OO′*-dimethyl dithiophosphato)molybdenum(III) and trichlorotris(tetrahydrofuran)molybdenum(III).

*Supplementary data available* (No. SUP 23470, 15 pp.): structure factors, thermal parameters, H-atom positions. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

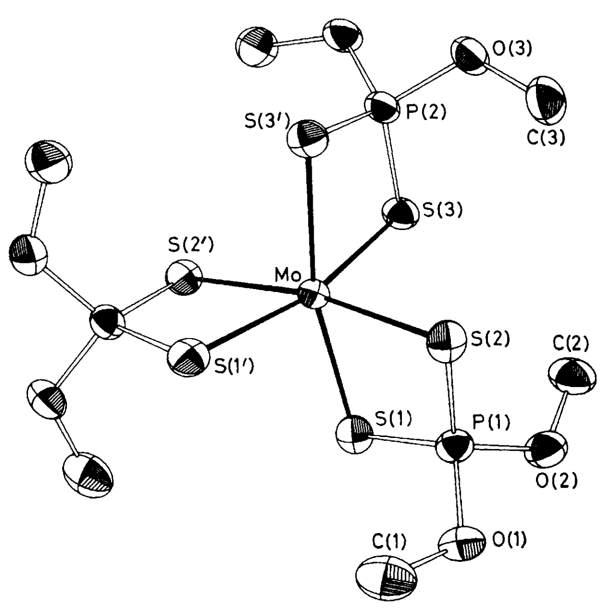

**Figure**. Stereochemical view of $[Mo\{S_2P(OMe)_2\}_3]$ showing the atom labelling scheme

Thus the complex overall reveals no unusual features and the greater stability of the molybdenum(III) monomer with dithiophosphinate rather than dithiocarbamate ligands is due to the larger bite angle of the dithiophosphinate providing great co-ordinative saturation. However, the complex $[Mo\{S_2P(OMe)_2\}_3]$ undergoes a range of oxidative addition type reactions which will be described in detail elsewhere.

## Experimental

All reactions were carried out under dinitrogen using dried solvents in conventional Schlenk apparatus. The complex $[MoCl_4(thf)_2]$ was prepared by the literature method,[4] and $[NH_4][S_2P(OMe)_2]$ used as purchased. Microanalyses were performed by Mr. and Mrs. A. G. Olney at the University of Sussex.

*Trichlorotris(tetrahydrofuran)molybdenum*(III).—Tetrachlorobis(tetrahydrofuran)molybdenum(IV) (5.0 g) was suspended in tetrahydrofuran (60 cm$^3$) and stirred with coarse tin powder (10 g) at room temperature for 20 min. The solution was filtered and any $[MoCl_3(thf)_3]$ on the sinter was freed from tin by washing through with dry dichloromethane. The solution was then evaporated at $10^{-2}$ mmHg ($0.136 \times 9.8$ Pa) to *ca.* 30 cm$^3$ and the complex filtered off as a pale orange crystalline material (3.4 g, 62%). The complex is best stored in a freezer and in the dark.

*Tris(OO'-dimethyl dithiophosphato)molybdenum*(III).—Trichlorotris(tetrahydrofuran)molybdenum(III) (1.0 g) and $[NH_4][S_2P(OMe)_2]$ (1.5 g) were stirred in methanol (40 cm$^3$) at room temperature for 1 h. The complex precipitated as a pinkish red solid, which was recrystallised as red needles from dichloromethane–diethyl ether or dichloromethane–Pr$^i$OH (0.69 g, 51%).

X-*Ray Crystal Structure Determination*.—*Crystal data*. $C_6H_{16}MoO_6P_3S_6$, $M = 565.38$, $a = 14.342(5)$, $b = 11.239(5)$, $c = 12.945(4)$ Å, $\beta = 97.12(1)°$, $U = 2\,070.44$ Å$^3$, $D_m$ (by flotation) $= 1.85(2)$, $Z = 4$, $D_c = 1.82$ g cm$^{-3}$, space group $C2/c$, Mo-$K_\alpha$ radiation, $\lambda = 0.710\,73$ Å.

Intensity data were recorded on a Nicolet R3/m automated diffractometer using graphite monochromatised Mo-$K_\alpha$ radiation. The crystal had dimensions $0.15 \times 0.31 \times 0.17$ mm. Intensities were measured by a $\theta$—$2\theta$ scan, with a $2\theta$ scan rate variable between 0.5 and 30.0° min$^{-1}$, scan length of 1.2°, a scan range of $0 < 2\theta < 45.9°$, and 10-s stationary background counts. Three reference reflections were monitored every 100 reflections. 2 453 Reflections were collected, of which 1 986 were considered observed $[F_o > 6\sigma(F_o)]$ and were used for the structure analysis. The data were corrected for background, attenuation, Lorentz and polarisation effects, and for absorption.

*Structure determination and refinement*. The position of the Mo atom was located from a sharpened Patterson map. All non-hydrogen atoms were located on difference-Fourier maps. Blocked full-matrix least-squares refinements were carried out on the positional and thermal parameters of all the non-hydrogen atoms. Least-squares refinement converged with $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.039$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{\frac{1}{2}} = 0.038$, where $w = 1/F_o^2$. Neutral atomic scattering factors for Mo, P, S, and C were taken from ref. 7 and for hydrogen from ref. 8. The Mo, P, and S scattering factors were corrected for real and imaginary components.[9] All calculations were performed on a Data General Nova 3 computer with 32 K of 16-bit words using the Nicolet SHELXTL interactive crystallographic package.[10]

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